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Mn K-EDGE X-RAY ABSORPTION SPECTROSCOPY (XAS) STUDIES OF $La_{1-x}Sr_xMnO_3$

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ABSTRACT

Systematic Mn K-edge x-ray absorption spectroscopy (XAS) measurements on samples of $La_{1-x}Sr_xMnO_3$, which are precursors to colossal magnetoresistive (CMR) materials, are reported. Detailed results on the edge or chemical shift as a function of Sr concentration (hole doping) and sample preparation (air vs oxygen annealed), are discussed. For comparison, a systematic XANES study of the Mn K-edge energy shift, denoting valence change in Mn, has been made in standard manganese oxide systems. Contrary to expectations, the variation in near-edge energies for Mn in $La_{0.725}Sr_{0.275}MnO_3$ were small when compared to the difference between that for manganese oxide standards of nominal valence of +3 and +4 (Mn_2O_3 and MnO_2).

INTRODUCTION

While $Ln_{1-x}A_xMnO_3$ systems are noted for their giant magneto resistance (GMR) behavior [1], the system $La_{1-x}Sr_xMnO_3$ is prototypical of colossal magneto resistive (CMR) materials as introduced by Asamitsu et al. [2]. This perovskite system exhibits unusual coupling which is presumed to depend on the mixed valent Mn^{+3}/Mn^{+4} lattice.

$LaMnO_3$, without an divalent ion or hole substitution for La^{+3}, exhibits ferromagnetism, insulator-metal transitions, and GMR, provided a sufficient proportion of Mn^{+4} is introduced by La or Mn deficiency [3]. Chemical substitution of La^{+3} by Sr^{+2} introduces holes into the e_g orbitals, that are mobile and mediate an interatomic ferromagnetic interaction between the Mn atoms and the material becomes ferromagnetic and metallic below T_C [4, 5].

Occurrence of ferromagnetism and metallic behavior of $La_{1-x}A_xMnO_3$ has been explained by Zener's double exchange mechanism [6] for the hopping of an electron from Mn^{+3} ($t_{2g}^3e_{2g}^1$) to Mn^{+4} (t_{2g}^3) via the oxygen. Double exchange and superexchange interactions [7] control the ferromagnetism in these systems. The Mn^{+3}-O-Mn^{+4} superexchange interaction is ferromagnetic, while that of Mn^{+3}-O-Mn^{+3} or Mn^{+4}-O-Mn^{+4} are not. There is also evidence, in the case of layered perovskite $La_{1.2}Sr_{1.8}Mn_2O_7$, under hydrostatic pressure, of exchange striction, which reflects the competition between super and double exchange [8].

The change in structural properties of $La_{1-x}Sr_xMnO_{3\pm\delta}$ as a function of oxygen partial pressure [9] indicate that the properties are strongly affected not only by the strontium content, x. but also by the oxygen nonstoichiometry, δ. It has been found that decreasing $P(O_2)$ yields smaller cation vacancy concentrations and smaller Mn^{+3}/Mn^{+4} ratio [10]. Undoped and Sr-doped $LaMnO_3$ exhibited reversible oxidation-reduction behavior. where the perovskites can be excess, stoichiometric or deficient in oxygen content depending on he specific condition. Metal vacancies are assumed for the oxygen excess condition and oxygen vacancies are assumed for the oxygen deficient condition. In high $P(O_2)$ region, metal vacancies on both La and Mn sites are the predominant defects [11].

The energy required, in X-ray Absorption Near Edge Spectroscopy (XANES), to excite a 1s electron to a delocalized p level at the Mn K-edge varies as the number of electron holes associated with the Mn atom changes. The calculated value of the K-edge for Mn mesh is 6539 eV. However, it requires more energetic photons to excite an electron away from the core potential as the positive charge on the Mn atom that absorbs the photon is increased. This effect manifests itself as a shift in the overall energy position of the absorption edge (called an edge shift) to higher energies with increasing net charge. For example, the Mn K-edge of MnO_2 (nominal valence Mn^{+4}) will have a shift to several eV higher energy when compared to that of Mn_2O_3 (nominal valence Mn^{+3}).

In order to quantify the energy shift of Mn in different oxide environments, we use a method involving the determination of an energy moment of the normalized absorption cross-section μ_0 and treating the absorption edge as a step function [12]. This method is more representative of overall charge density at the manganese atom in each compound than other approaches which attribute detailed meaning to isolated or individual features of the spectrum [13]. By taking an systematic overall approach, which is more akin to the concept of valence, the details of spatial charge distribution and electronic hybridization as well as complicated pre-edge structure may be avoided. In this manner, the edge shift observed for the Mn_3O_4, Mn_2O_3, $La_{1-\delta}Mn_{1-\delta}O_3$ and MnO_2 are real and reflect a difference in the Mn valence.

Formal valence is only one factor contributing to the charge environment of the Mn atoms. Other factors such as coordination numbers and the relative electronegativities strongly influence the actual charge environment in solids. Qualitatively, the shape of the XANES signal can be correlated with the coordination number of the element of interest [14].

SAMPLE PREPARATION AND EXPERIMENT

$La_{1-x}Sr_xMnO_{3+\delta}$ samples were synthesized by co-precipitation of carbonates from a solution of the corresponding nitrates. Starting materials consisted of the high purity oxides La_2O_3 (Johnson-Matthey REacton, 99.99%) and MnO_2 (Johnson-Matthey Puratronic, 99.999 %); $SrCO_3$ (Johnson-Matthey Puratronic, 99.999%) was used as a Sr source. La_2O_3 was prefired in flowing oxygen at 1000 °C for several hours to decompose residual carbonates, and the MnO_2 was treated in flowing oxygen at 425 °C and slowly cooled (1 °C/min) to room temperature. $SrCO_3$ was used as-received. Prefired MnO_2 was dissolved in concentrated HCl and the solution was slowly evaporated to dryness. The residue was then redissolved in a minimum of H_2O. To remove chlorides, concentrated HNO_3 was added to the solution, which was again heated to dryness. The resulting pink solid was dissolved in H_2O. Concentrated

nitric acid was slowly added to a stoichiometric mixture of $SrCO_3$ and the prefired La_2O_3. This solution was then added to the manganese solution and the cations coprecipitated by slow addition of a saturated $(NH_4)_2CO_3$ solution. The supernatant was then decanted and the precipitate dried and pulverized to yield a fine, light pink precursor powder. The precursor powder was slowly heated (0.5 °C/min) in flowing oxygen to 250 °C to remove water. The temperature was then ramped at 10 °C/min to 1000 °C and held at this temperature for 10 hours before rapidly cooling to room temperature. The resulting material is an extremely fine black powder.

The XANES measurements were made in step scan mode in transmission geometry at beamline X6B at the National Synchrotron Light Source (NSLS, BNL). Si(111) crystals are used to monochromatize the synchrotron radiation. The $\Delta E/E \approx 10^{-4}$. Manganese mesh spectra was recorded simultaneously (in the backchannel) so that the edge position of the manganese could be calibrated. The inflection point in the first resolved peak of the manganese mesh was chosen to be the zero of the energy scale. This is relatively easy to locate and reproduce, since the derivative of the spectrum has a sharp peak at that point. In this manner, the edge shifts (the change in valence of the Mn) of the Mn K-edges for all manganese containing systems could be compared.

RESULTS AND DISCUSSION

The XANES spectra shown in figure 1 were taken at room temperature. A standard manganese mesh spectrum was taken simultaneously so that the backchannels could be lined up on top of each other and the front channel (sample) shifted by the same amount. The inflection point in the first resolved peak of the standard Mn mesh of the near edge was chosen to be the zero of the energy scale. This is relatively easy to locate and reproduce, since the derivative of the spectrum has a sharp peak at that point. Therefore, the edge shift observed for the Mn_2O_3 $La_{0.725}Sr_{0.275}MnO_3$, and MnO_2 in figure 1, are real and reflect a difference in the Mn valence, which are, nominally +3, +3.275 and +4.

All of the spectra from the Mn oxide standards, exhibit different shapes which are indicative of their respective Mn-oxygen coordination number or the position of the Mn in the different crystal structures. It has been shown [15] for transition metal oxides that the various shapes of the transition metal K-edge reflect the coordination number of the transition metal with oxygen. For example the shape of the Mn K-edge of Mn_2O_3 is like that of the other 4-fold transition metal elements with +3 octahedral coordination with oxygen.

From previous work [16] we have found that the shape of the Mn K-edge of $La_{1-x}Sr_xMnO_3$ is exactly the same for x = 0.000 and 0.275, so that one may infer that with the addition of Sr, the electronic configuration of Mn remains intact. The slight shift (< 0.2 eV) of the Mn edge to higher energy for $La_{0.725}Sr_{0.275}MnO_3$ indicates an increase of the valence on the Mn atom. For the standard Mn oxide compounds, as shown in figure 1, the different shapes of the Mn K-edges are more distinguishable and the edge shifts are much larger (> 2 eV) indicating very different coordination numbers and Mn electronic configurations.

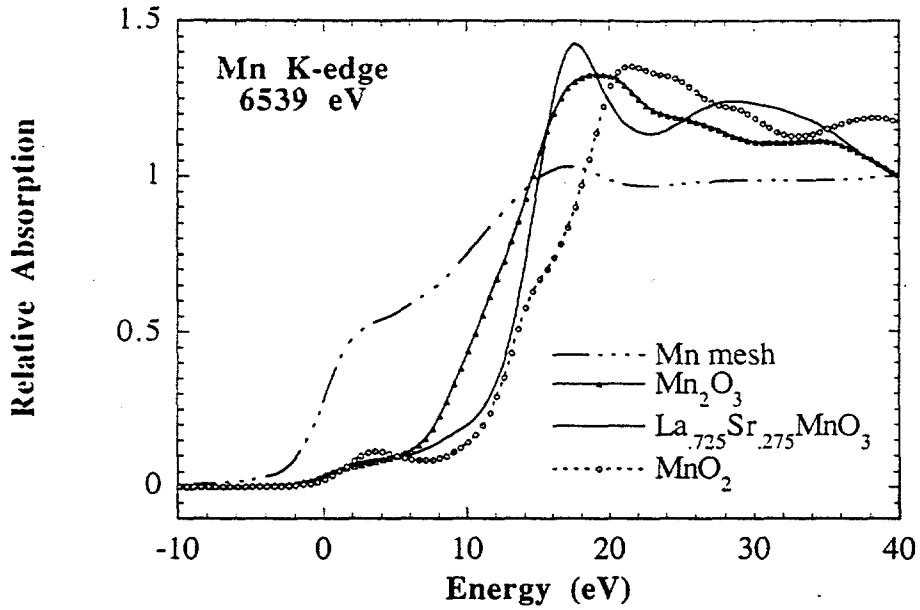

Figure 1. Mn K-edge of room temperature XANES comparing $La_{0.725}Sr_{0.275}MnO_3$ with a nominal Mn valence of +3.275 to standard Mn mesh, Mn_2O_3 with a nominal Mn valence of +3, and MnO_2 with a nominal valence of +4.

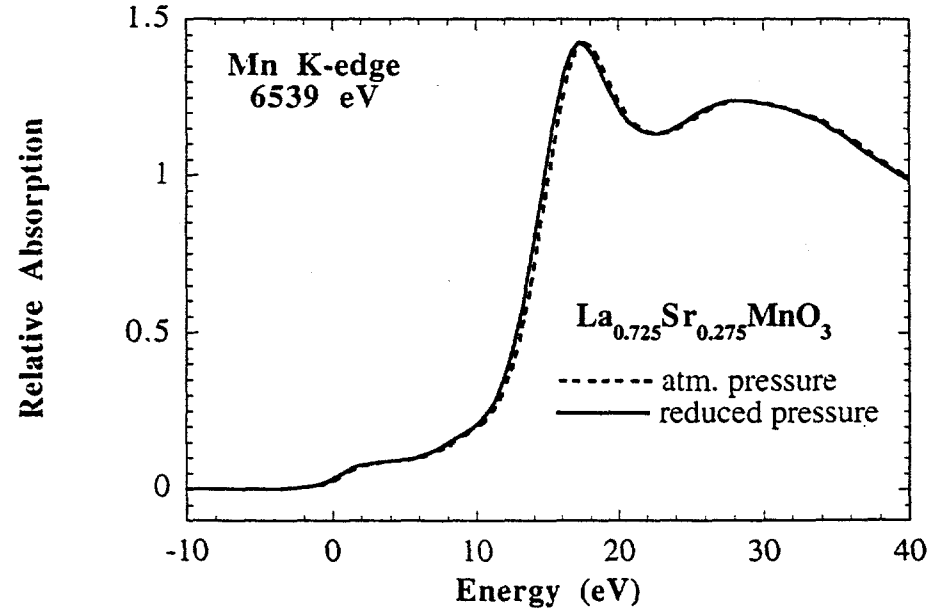

Figure 2. Comparison of Mn K-edge spectra of $La_{0.725}Sr_{.275}MnO_3$ prepared at atmospheric and reduced pressure.

Figure 2, shows an edge shift to higher energy and therefore higher Mn valence for Mn K-edge spectra of $La_{0.725}Sr_{0.275}MnO_3$ samples produced at atmospheric pressure and reduced

pressure, respectively. Nominally, $La_{0.725}Sr_{0.275}MnO_3$ has a Mn valence of +3.275. However, figure 2 indicates that the sample prepared at atmospheric pressure has an overall Mn valence slightly higher than that of the sample produced at reduced pressure. This suggests that the sample produced at atmospheric pressure has less oxygen in its system and a higher Mn^{+4} content than that produced at reduced pressure.

It has been shown by Mahendiran, et al. [17] that reduced pressure $La_{1-\delta}Mn_{1-\delta}O_3$ and hole doped $LaMnO_3$ exhibit cation vacancies as opposed to anion vacancies. In Mahendiran's experiments the Mn^{+4} content of the samples was determined independently by redox titrations methods. In the high $P(O_2)$ region, metal vacancies on both La and Mn sites are the predominant defects [11].

It has been suggested that in the perovskite system $LaMnO_3$, the origin of Mn^{+4} cannot be due to oxygen excess since the perovskite structure cannot accommodate excess oxygen and that high percentages of Mn^{+4} in $La_{1-\delta}Mn_{1-\delta}O_3$ materials, are created by the random presence of cation vacancies in both La and Mn sites [18]. In fact, a large suppression of magnetoresistance due to cation disorder is evidenced [19] in the CMR precursor systems, indicating that the cation disorder and size effects in magnetoresistive manganese oxide perovskites is an important consideration.

To summarize, we have shown that the Mn K-edge XANES, gives information regarding the valence changes on the Mn and therefore the electronic configuration in manganese oxides as a function of hole doping as well as whether the sample is produced in atmospheric or reduced pressure. The Mn K-edge XANES is very sensitive to hole doping, indicating that the Mn valence in $La_{1-x}Sr_xMnO_3$ increases as a function of Sr doping and also to the increase or decrease in the oxygen content, as shown in the difference in the XANES at atmospheric and reduced pressure. The XANES edge shifts maybe be correlated to the Mn^{+4} content through independent means (redox titration or density measurements for the oxygen content).

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REFERENCES

1. C.N.R. Rao, Chem. Commun. 2217 (1996).
2. A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, Nature **373**, 407 (1995).
3. A. Arulraj, R. Mahesh, G.N. Subbanna, R. Mahendiran, A.K. Raychaudhuri, C.N. R. Rao, J. Solid State Chem, **127** 87 (1996).
4. C.N. R. Rao, A.K. Cheetham, R. Mahesh, Chem. Mater. **8** 2421 (1996)
5. J.H. van Santen, G.H. Jonker, Physica **16** 599 (1950).
6. C. Zener, Phys. Rev. **82** 403 (1951).

7. J.B. Goodenough, Prog, Solid State Chem. **5** 149 (1971).
8. D.N. Argyriou, J.F. Mitchell, J.B. Goodenough, O. Chmaissem, S. Short, and J.D. Jorgensen, Phys. Rev. Lett. **78** 1568 (1997).
9. H.U. Anderson, J. H. Kuo and D.M. Sparlin, in: Proc. First Intern. Symp. Solid Oxide Fuel Cell (Electrochem. Soc., 1089) pp. 111-128.
10. John F. Mitchell, D.N. Argyriou, C.D. Potter, D.G. Hinks, J.D. Jorgensen, and S.D. Bader, Phys Rev. B **54**, 6172 (1996).
11. J.H. Kuo, H. U. Anderson, and D.M. Sparlin, J. Solid State Chem. **83**, 52 (1989) and J.H. Kuo, H. U. Anderson, and D.M. Sparlin, J. Solid State Chem. **87** 55 (1990).
12. E.E. Alp, G.L. Goodman. L. Soderholm, S. M. Mini, M. Ramanathan, G.K. Shenoy and A.S. Bommannavar, J. Phys.: Condens. Matter **1** 6463 (1989).
13. M. Croft, D. Sills, M. Greenblatt, C. Lee, S.-W. Cheong, K.V. Ramanujachary and D. Tran, Phys. Rev. B **55**, 8726 (1997).
14. M. Lenglet, J. Delepine, J. Lopitaux, J. Durr, J. Kasperek and R. Bequignat, J. Solid State Chem. **58**, 194 (1985).
15. G.S. Knapp, B.W. Veal, H.K. Pan and T. Klippert, Solid State Comm. **44** 1343, 1982.
16. S.M. Mini, John Mitchell, D.G. Hinks, C.W. Kimball, P.A. Montano, P.Lee, D. Rosenmann, A.V. Tkachuk, and A. Udani, Mat. Res. Soc. Symp. Proc. **437**, 85 (1996).
17. R. Mahendiran, S.K. Tiwary, A.K. Raychaudhuri, T.V. Ramakrishnan, R. Mahesh, N. Rangavittal, and C. N. R. Rao, Phys. Rev. B 53, 3348, (1996).
18. J.A.M. Van Roosmalen, E.H.P. Cordfunke, R.B. Helmholdt, and H.W. Zandbergen, J.Solid State Chem. **110**. 100 (1994) and J.A.M. Van Roosmalen and E.H.P. Cordfunke J.Solid State Chem. **110**, 109 (1994)
19. Lide M. Rodriguez-Martinex and J. Paul Attfield, Phys. Rev. B **54**, 15622 (1996).